PE-3842

PATENT SPECIFICATION (11) 1 569 138

1 569 138

(21) Application No. 43298/76 (22) Filed 19 Oct. 1976 (19)

(31) Convention Application No. 49197 (32) Filed 24 Oct. 1975 in

(33) Greece (GR)

(44) Complete Specification Published 11 Jun. 1980

(51) INT. CL.[3] D21C 1/04
C13K 1/02 13/00

(52) Index at Acceptance
D2W 2 3A12B 3A1A 3A1B 3A1C 3A1X 3A2A
3A4A 3B1
C2S

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(54) PRODUCTION OF MONOSACCHARIDES AND A CELLULOSIC-RICH MATERIAL FROM STRAW

(71) We, GEORGE NICOLAS VALKANAS of 14 Constantinopoleos Street, Amaroussion, Greece; DEMETRUIS GEORGE ECONOMIDIS of 7 Agiouthoma Street, Amaroussion, Greece; and EMMANUEL GEORGE KOUKIOS of 14 Ilision Street, Athens, Greece; all Greek citizens, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a new method for the profitable utilisation of cellulosic agricultural by-products. It refers particularly to a new method for the profitable utilisation of straw to produce useful products such as pulp, cellulose of desirable purity and fermentable sugars. The present invention relates especially to a process for producing the cellulosic product (pulp or pure cellulose) and the fermentable sugars simultaneously, that is by making from each part of the raw material a product of optimal quality and yield. Thus, the utilisation of straw is substantial and much needed materials are producted, such as pulp for making paper, grades of cellulose and fermentable sugars suitable for use in the cultivation of microbes for the production of single cell proteins for cattle feed and human use. The present invention apart from its technological value has considerable economic and social importance, since about 60 - 70% by weight, of the annually produced agricultural products are cellulosic by-products.

In a large number of these agricultural by-products, the cellulose is of the type which can be used in several industrial applications (for example for the production of chemical pulp) and according to the present process can be obtained in a high yield and purity or in the form of widely used industrial products together with the other non-cellulosic constituents it contains. If the present process was used on a wide scale, agricultural by-products could become a more important source of valuable materials.

The present invention relates to a process for the production of monosaccharides and a cellulosic-rich material which comprises subjecting straw for 10 - 180 minutes to a selective prehydrolysis treatment in the presence of one or more acid catalyst at a temperature of from 100 to 160°C under pressure until the easily hydrolysable constituents of the straw such as pentosans, starch and hemicelluloses are converted substantially into monosaccharides in a yield representing 15 - 23% by weight of the straw, and until a residue rich in cellulose is obtained in a yield representing 68 - 76 % by weight of the straw, said residue being suitable for processing to chemical pulp and to pure cellulose.

All the percentage figures given herein are used on a weight basis, unless otherwise indicated.

Cereal straws form a main part of the annually produced agricultural by-products, being

produced in approximately twice the quantity by weight, of cereal grains. Of main interest, for use on this present invention, and for other reasons which will become evident below, are varieties of straw from wheat, barley and rice which have the composition shown in the following table.

TABLE

Average Composition of straw, % (w/w)	Wheat	Barley	Rice
Pentosans	22 - 25	25 - 27	23 - 26
Hemicelluloses	19	15	-
Alpha-Cellulose	38 - 41	40 - 41	42 - 44
Lignin	15 - 17	17 - 18	12 - 14
Ash	6 - 7	3 - 5	14 - 16

Alfalfa or rice straw are particularly suitable for use in the present invention.

According to the present process, the pentosans in the straw are subjected to a partial or complete hydrolysis, in such a way, that the hydrolysis product essentially consists of pure monosaccharides and of a solid residue which is suitable for the production of high quality chemical pulp or cellulose of high grades. The partial hydrolysis, being combined with the production of chemical pulp, has to satisfy several requirements. The cellulosic hydrolysis product should comprise a pulp of high quality suitable for use in the paper industry, and this, which is well known to the specialists in the field, depends on many, mostly controversial, factors. Thus, the quality of pulp basically depends on the structure of the cellulosic fibres but also on the presence of hemicelluloses which substantially improve the pulping properties. In the case of pulp from straw, the presence of hemicelluloses is also of fundamental importance for preserving the structure of the fibres since the hemicelluloses contribute to the protection of the fibres from the chemicals generally used in pulping. It is known that straw fibres are rather short, having a mean length of 1-1.5 mm compared to a mean length of 4-5 mm for wood fibres. On the other hand, straw fibres show better orientation and cohesion, qualities which, in the presence of hemicelluloses, compensate for the shortness deficiency and therefore a pulp of high quality can be produced.

In one embodiment of the process according to the present invention, the cellulosic residue has a content of 52-58%, by weight, alpha-cellulose and the acid catalyst is an inorganic or organic acid.

The cereal straws are known to be rich in pentosans which, if they remain in the final pulp, adversely affect its quality. Thus, the pentosans should be removed before pulping but at the same time ensuring the cellulosic residue is of the desired quality, as indicated above. Additionally, the pentosans should be quantitatively hydrolysed to monosaccharides which are sufficiently free from inhibiting compounds so as to be suitable for fermentation processes. According to the above the hydrolysis treatment should be selective in that the easily hydrolysable constituents of the straw are converted mainly into monosaccharides. This is one of the fundamental features of the present invention. The concentration of the acid catalyst is kept low and the temperature selected so that the hydrolysis treatment is for 10 - 180 minutes. Suitable catalysts are strong inorganic and organic acids for example, sulphuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$), phosphoric acid (H_3PO_4), sulphurous acid, chloroacetic acid ($ClCH_2COOH$), *p*-toluene sulphonic acid (*p*-CH_3-C_6H_4-SO_3H), of the above catalysts, HCl, H_3PO_4 and HNO_3 and mixtures thereof give better results as regards the quality of the hydrolysis sugars obtained. Phosphoric acid is a nutrient in the fermentation of sugars while nitric acid is useful because during fermentation it is converted to a nitrogeneous nutritive salt and because when it is used as a catalyst, partial oxidation of sugars and lignin occurs, the traces of partial oxidation products formed being useful in the fermentation process. The concentration of the acid catayst is kept between 0.1 - 1 % by weight based on the total acid solution used and the temperature between 100 - 160°C preferably between 130 - 150°C.

The acids used as catalysts in the prehydrolysis behave as usually happens in these types of reactions, according to their molarity and not to their normality. If the action of HCl is compared with that of H_2SO_4 (and also with other acids having a higher molecular weight), it can be seen that smaller amounts of HCl are required to produce the same effect. Furthermore, it is more preferable to have chlorides than sulphates in the sugar solution during its subsequent fermentation. The yield of the proteinic mass produced from the microbial growth when the yeast *Candida utilis* for example; is used, amounts to 60 - 65 % by weight based on the sugars consumed in the substrate. The highest yields are obtained

when one of the acids HCl or HNO_3 or H_3OP_4 is used as a catalyst in prehydrolysis.

Using the present process, not only are fermentable sugars produced, but also a cellulosic residue of high quality. Thus, the present process is continuous and bi-directional in that two distinct operations, which were previously considered to be contradictory (namely the production of fermentable sugars and the production of chemical pulp) may be efficiently carried out. Since both these products are economically important the fact that the process is bi-directional is very important. Paper pulp of high quality can be produced, using as raw material the cellulosic residues from hydrolytic pretreatments, which have already produced 15 to 23 % by weight based on the initial straw of monosaccharides. Since these sugar solutions are also useful products the maximum possible sugar yield should be preferred each time. Other factors which influence the hydrolysis are the temperature and the pressure at which the process occurs. Hydrolysis treatment at a temperature between 120 - 140°C is completed in a short time of 10 - 60 minutes and because of that and the treatment under pressure, the structures of the cellulosic fibres and of the hemicelluloses are preserved. The yields of sugars after the hydrolysis treatment as above are independent of the processing temperature, and are as follows: xylose 67 - 75 % arabinose 10 - 18 %, mannose 1.2 - 5 %, glucose 5 - 12 % and galactose 2 - 4 % all the percentages being by weight. This sugar mixture is a very suitable nutrient for microbes used for the production of protein feeds, the monosaccharides apart from arabinose, being completely consumed. Arabinose is exceptional because although it resists fermentation, it does not act in any way as an inhibitor. Under the above conditions, some furfural is produced together with the sugars in a concentration of 0.02 - 0.25 g/lit in the final sugar solution. The above monosaccharides are the complete hydrolysis products of the pentosans and to a small extent the hydrolysis products of hemicelluloses. After this, the cellulosic residue for pulping has the composition: alpha-cellulose 52 %, lignin 23 %, hemicelluloses 12 %, extractives and ash 13 %, all the percentages being by weight.

We have also discovered that the cellulosic residue can be successfully used, under specified conditions, in the production of chemical pulp. In particularly, we have developed methods for the production of all basic commerical types of pulp, that is kraft, sulphite, and modified kraft which are characterised by high mechanical strength suitability in paper making and compatibility in paper making with the same or different types of wood pulp. Other methods are substantially different from the processing and the technology used in pulp production from wood, and according to our knowledge, they have not been used before in that form or in such a relation for the production of pulp from this special quality of prehydrolysed straw. The prehydrolysed straw, which is the starting material for pulp production according to the present invention, as stated before, is an entirely different material to wood and a substantially different material to straw, and to some types of straw, subjected to pre-treatment of a hydrolytic character before the production of rayon viscose, or low quality paper, according to the literature.

In our new starting material the cellulose fibres are kept in their natural state without fragmentation of the cellulose molecules and disturbances in the orientation of the fibres.

Thus, the present invention also relates to a process for the production of chemical pulp wherein the cellulosic residue of the straw prehydrolysis in which the yield of sugars was 17 - 20 % by weight, is treated with an alkaline solution of sulfite salts, and then heated within two hours up to 150 - 160°C and maintained at that temperature for 5 - 6 hours.

The alkaline solution of sulphite salts preferably contains 255 kg Na_2SO_3 and 85 kg NaOH per ton of dry pulp.

The present invention also relates to a process for the production of kraft pulp wherein the cellulosic residue of the straw prehydrolysis in which the yield of sugars was 15 - 19 % by weight is treated with a kraft pulping solution containing Na_2S and NaOH and with a pulping solution in which Na_2S and NaOH are partially replaced by Na_2SO_3 and then heated up to 150 - 160°C and maintained at that temperature for 4 - 6 hours.

The kraft pulping solution preferably contains 125 kg Na_2S and 260 kg NaOH per ton of dry pulp.

Preferably, the pulping chemicals Na_2S and NaOH are partially replaced by Na_2SO_3 in a quantity of 0.1 - 30 % by weight. Our prehydrolysis treatment is very successful in that the prehydrolysed product has a degree of polymerisation similar to that of the starting straw of 800 - 820 glucose units compared with a degree of polymerisation of 500 - 600 glucose units obtained when a non selective straw hydrolysis treatment is used. The cellulose and lignin contents are substantially higher, amounting to 50 - 54 % and 22 - 24 % by weight respectively, while other constituents such as hemicelluloses are present in about normal amounts. Thus, in pulp production conditions are required which preserve the qualities and the quantities of alpha-cellulose and hemicelluloses. The prior art methods of pulping are therefore not suitable for use in the present case in the form they are used for wood but, as shown in the examples of this invention can be substantially revised. A high quality paper

pulp can be produced according to the kraft method from a prehydrolysis residue after only comparatively mild hydrolytic treatment of straw, that is, after the production of no more than 15 - 18 % by weight of monosaccharides, based on the straw. This is the result of the high penetration efficiency of the chemicals used in this method, together with the absence of a great part of the hemicelluloses from the cell walls. On the other hand, paper pulp, of exceptional quality can be produced from prehydrolysis residues according to the sulpite and modified kraft (Example 12) methods, after a stronger hydrolytic treatment of straw, wherein upto 20 % of monosaccharides by weight of the straw, have been produced.

This difference can be explained on the basis of the greater selectivity of delignification presented by the latter two methods.

The present invention also relates to a process for the production of pulp from our prehydrolysed straw, using a chlorine method which is entirely different from the other chlorine methods for pulping and for the well-known "POMILIO" method for the production of pulp from straw. According to the present method, the chlorine treatment is subsequent to the useful acidic prehydrolysis and does not require an alkali wash in between. Thus, the present chlorine method has fewer steps of treatment and in spite of the very simplified procedure gives impressive results in yield and quality of pulp. The prehydrolysed straw obtained (that is, the residue of a hydrolytic treatment whereby 15 - 23 % monosacchrides (by weight of the straw were produced) after pressing and draining off of the sugar solution, with moisture between 60 - 100 % of dry matter, is directly subjected to chlorine treatment with chlorine gas. The chlorine is absorbed readily in quantities between 18 % and 23 %, by weight, of the prehydrolysed straw in a reaction which, although exothermic, is readily controlled of a temperature between 30° and 40 °C.

The absorption of chlorine leads to the formation of pink colored chlorolignins, the coloration of which at the end of the reaction is spread homogeneously all over the chlorinated mass. The development, thus, of the pink coloration can be used to follow the chlorination procedure. Another significant advantage of using this method of pulping prehydrolysed straw, is that even after a prehydrolysis producing 20 - 23 % monosaccharides by weight of the initial straw, (that is, a yield not permissible when using conventional methods of pulping) the residue can be easily chlorinated and gives a pulp of exceptional quality.

Delignification by chlorine is very effective and as it was developed by Pomilio and others, a special method for the pulping of straw. These chlorine pulping methods, however, are impaired by the liberation of substantial quantities of hydrochloric acid which makes the processing acidic in nature, in which the hydrophobic straw is much more resistant and can stand these conditions better than the prehydrolysed straw. The present case, therefore, requires different utilisation of the chlorine reagent for selective delignification without damaging the structure of the fibre and the hemicelluloses. After extensive studies on existing possibilities procedures of treatment, we were successful in developing a special method and conditions of processing satisfying all the above requirements. Our special method consists of introducing the chlorine into horizontal slowly rotating reactors or vertical slowly stirred reactors containing the residue from a straw prehydrolysis, as described before, having produced 15 - 23 % and preferably 20 - 23 % monosaccharides by weight of straw until up to 20 % by weight of chlorine, based on the prehydrolysis residue treated is absorbed. The product is then washed with water and alkaline solution until neutral. Generally, to obtain a pulp of improved quality, the residue from straw prehydrolysis is washed with a 1 - 3 % solution of NaOH before pulping.

After obtaining a satisfactory and uniform chlorination, the processed mass may be washed successively with water, 2 % sodium hydroxide solution and again water. Generally, the chlorination lasts 30 - 60 minutes and the subsequent washing should preferably be fast, using large volumes of water. The residue from the straw prehydrolysis may be introduced into the chlorination reactors in the form of a compressed hydrophilic mass and does not require a prewashing with dilute sodium hydroxide as in industrial practice for straw when the Pomilio process is used. The yield in dry pulp is between 50 - 51 % based on the initial straw.

Although it is preferred to use horizontal or vertical reactors for chlorine delignification it is also possible to use chlorination towers in which the chlorine gas passes in a direction counter-current to that of the moist residue from the straw prehydrolysis which is introduced at the top of the reactor. We have calculated that the time required for the prehydrolysed straw to fall from the top to the bottom (i.e. the time of straw-chlorine contact) should be reduced considerably with respect to that required using the known towers used in the Pomilio process. On the other hand, the introduction of chlorine needs special care and dilution with air. In the line of such improvements the pulp obtained is satisfactory both in quality and yield.

The types of pulp produced in accordance with the above treatment show satisfactory

mechanical and paper making properties compared with the best such qualities produced from wood. In addition, high purity pulps are obtained which may be decolorised with calcium hypochlorite in a mild treatment resulting in a weight loss of only 2-3 % by weight. This may be compared with losses of 6 - 10 % by weight for Pomilio straw pulp and 5 - 8 % by weight for pulp from wood. Thus, the yield in pulp improves favorably between straw and hydrolysed straw. In the following Table are given certain results after testing the paper making characteristics and the mechanical properties of the pulps obtained from prehydrolysed straw according to our process.

The present process is not only of technological success but also substantially decreases the costs of production. This is because both fermentable sugars, and a cellulosic residue suitable for chemical pulp formation are produced, and furthermore, there is a reduction in the industrial installations required.

TABLE

Pulping Method	Kraft		Alkaline Sulphite		Chlorine	
Freeness in Schopper-Reigler (SR°)	40	60	40	60	40	60
Breaking length(m)	5800	6500	6000	7300	6900	8000
Burst factor	30	56	28	45	26	48
Tear factor (dm^2)	70	52	65	40	73	45
Folding number (No. of double folds)	450	990	500	1100	780	1800

The production of pulp from wood or straw, because of the starting material used and the volume of the wastes produced generally, requires large industrial installations, which are expensive. Additionally, in most countries, it is necessary to use installations for the purification and disposal of the wastes produced and for recycling of cooling and processing water. This substantially increases the cost of processing and of the installations themselves.

By using the process of the present invention, there are not such pressing problems. The industrial waste formed from both lines of processing, that is the hydrolysis and pulping lines, amounts to about 30 % of the organic matter. Using the prior art processes, however, about 60 % of the organic matter is lost as waste. In addition to this, the organic wastes produced by this method contain 60 - 70 % lignin, that is, they have a high thermal value so that by condensing to 50 % solids, they burn easily in ordinary incinerators. In our chlorine method, lignin can be easily precipitated by acidification from the waste liquors of the alkali extraction following chlorination. The yield of the lignin is about 80 % by weight of the theoretical yield, and the lignin is suitable for a variety of uses according to known methods. Thus, in accordance with the present invention relating to the utilisation of straw, there is obtained a successful separation of monosaccharides from the pentosans, the pulp and the lignin. Thus, straw utilisation can be optimised whilst overall pollution may be decreased.

As is specified, by using the present invention, the basic machinery required for pulping is substantially reduced since the starting material is condensed by 25 - 30 % and the time for processing reduced by 35 - 40 %. Thus, the industrial installations required are reduced in volume by about 50 % as compared with those needed for the previously used wood pulping methods. In addition, water can be significantly economised because the effluents of the sugar fermentation plant contain 1 - 3 % of organic matter which is an acceptable purity for utilising these effluents in pulp washings. One of the advantages of the present invention in the utilisation of cereal straws is the reduced cost of processing and the reduced cost of the installations themselves.

The prehydrolysis treatment may be carried out in a vertical reactor which is loaded by a known method, for example, the procedure of loading wood for pulping. Alternatively, horizontal reactors may be used through which is passed a line of loaded carriages, so that loading and unloading the reactor is a fast operation hence enabling the reactor to be used more efficiently. After the prehydrolysis treatment, the prehydrolysed straw may be brought into a tank to drain the sugar solution and is then placed in another tank to be washed with water. This is usually followed by compressing at a pressure of 20 - 30 atm from which the prehydrolysed straw is obtained advantageously in bales having a retained moisture content of 40 - 50 % by weight. The compressed product may be directly utilised for pulping. In the case of chlorine pulping an alkali wash with 1 to 3 % NaOH solution before pressing may sometimes be advantageous for improving the colour of the finished pulp.

In one embodiment of the process according to the present invention, the cellulosic

residue, after the prehydrolysis treatment is washed with water and/or with a 1 - 3 % by weight sodium hydroxide solution and thereafter is compressed to a product having a moisture content of 40 - 50 % by weight. The solution obtained after hydrolysis, the washing solution and the solution obtained after compression may then be mixed to form a solution having a concentration of 1.2 - 5 % by weight in sugars which after adjusting to the original catalytic strength is recycled as a whole or partly as hydrolysis solution until a final concentration of 6 - 8 % by weight in sugars, is obtained and 90 - 95 % of the sugars in the final concentrated solution are monosaccharides.

In the hydrolysis procedure water is used in a quantity of 5 - 8 times the weight of the straw. A yield of from 15 to 23 %, of sugars are obtained from the hydrolysis which after the necessary washing of the cellulosic residue make solutions containing some 1.2 - 5 % sugars. If the sugars are to be used for fermentation purposes, higher sugar concentrations (between 4 - 6%) are desirable. We have found that the sugar solutions can be recycled to concentrations of 6 - 8 % by weight without any significant losses in sugars or destruction of the sugar composition.

In the prehydrolysis installations, all surfaces contacting the sugar solution should be resistant to the acidity of the solutions because metallic impurities such as Fe, Ni, Co, and Mn, when in solution inhibit fermentation of the sugar used as a substrate by microbes for producing single cell proteins. All metallic surfaces in contact with the solution must therefore be covered or lined with ceramics or with a plastics material suitable for the purpose.

In a partly different adaptation of the prehydrolysis procedure, the cellulosic residue, after processing in batch reactors, is pressed to produce a sugar solution of high sugar concentration (up to 5 %, by weight). The pressed mass is subsequently washed with hot water and the new resulting dilute sugar solution, obtained after pressing, is recycled as the process solution. Using such a sequence, production of a concentrated solution of sugars is possible.

Under stronger conditions of temperature or time of processing, the hydrolysis of straw proceeds to a higher degree which is characteristic and at which the reducing sugars produced amount to 29 - 31 % of straw weight. The cellulosic residues after this severe hydrolysis show a certain resistance to further hydrolysis and appear to have attained a stable structure which on analysis was found to have the composition: alpha-cellulose 57 %, hemicelluloses 10 %, lignin 22 %, other constituents 11%. The sugar solution obtained had the composition : xylose 70.3 %, mannose 2.1 %, ribose 1.4 %, arabinose 17.6 %, glucose 6.8 % and galactose 1.8 % and it was especially suitable as a fermentation substrate for microbes for producing proteins. The cellulosic residue thus obtained is not very suitable for processing alone to pulp of good paper making characteristsics. Using mixtures, however, of that pulp with mechanical wood pulp 50 : 50 (w/w) products having excellent paper making properties are obtained. On the other hand, this pulp prepared under selective conditions, may have a high alpha-cellulose content, that is 95 - 96 % by weight which makes its quality very suitable for the production of rayon, of Cellophane ("Cellophane" is a Registered Trade Mark) and substituted cellulose products.

According to the present method, the end products obtained are pulp and microbe cultures (produced using the sugar solution as a substrate) in approximate yields of 43 - 51 % and 18 % respectively both of which are known to be basic market products of high value and which represent a utilisation of straw of 59 - 69 % by weight. This utilisation of straw is higher than could be obtained by other previously known methods. If lignin is also considered, the maximum total yield of useful products is 85 % by weight, based on the initial dry straw.

The invention is illustrated by the following Examples, in all of which the prehydrolysis treatment time was from 10 to 180 minutes.

Example 1

Prehydrolysis of wheat straw was carried out in an apparatus, lined internally with Teflon ("Teflon" is a Registered Trade Mark) the apparatus being capable of working under pressure and being equipped with recording instruments for temperature and pressure. The apparatus consisted of a 5 lit reactor, a preheating unit used to heat up the process water solution, and following the reactor, a pressure and flow regulating valve system and a graphite heat exchanger. The following methods were used:

a) 0.8 kg of dry straw was introduced into a cage of Teflon in the reactor. Through this were introduced 10 lit of 0.3 % aqueous HCl, under a pressure of 5 - 5.5 atm. at a temperature of 145°C and at a flow rate of 0.55 litres/minute. The reactor was then purged with dry steam (i.e. supersaturated vapour was used to purge the material) filled with hot water at a temperature of 120 - 130°C and purged again with dry steam. After that, the residue was taken out and pressed at 25 kg/cm^2 to form a product having a moisture content

of 45 - 50 % by weight. From the apparatus and the press were collected a total of 13.4 litres of solution containing 1.34 % by weight reducing sugars, equal to a yield of 23 % by weight of the straw. the solution obtained had the composition : xylose 74.3 % mannose 5.2 % arabinose 11.8 % glucose 5.9 % galactose 2.9 % and furfural 0.16 g/lit. The cellulosic residue had a dry weight of 0.545 kg, that is a yield of 68.2 % by weight and had the following composition : alpha-cellulose 53.1 % hemicelluloses 12.6 % lignin 22.1 % ash which extractables 12.2 % and a degree of polymerisation of 805 glucose units.

b) 0.8 kg of dry straw was placed into the reactor of the apparatus and subjected to a hydrolysis treatment as described above, using a solution containing 0.5 % HCl at a temperature of 145°C introduced at a flow rate of 0.95 lit/minute. After purging with steam, washing with hot water, purging again with steam, and pressing the residue, there were collected 13.5 litres of solution containing 1.32% by weight of reducing sugars corresponding to a yield of 22.7 % by weight. The cellulosic residue had a dry weight of 0.550 kg, that is, a yield of 69.4 % by weight of the original straw and a degree of polymerisation of 792 glucose units.

c) In a hydrolysis treatment of 0.8 kg dry straw as described above using a 0.3 % HCl solution, at a temperature of 145°C and a flow rate of 1.0 lit/minute, there were collected: a solution containing 1.09 % reducing sugars, by weight, that is a yield of 18 % by weight of the straw, the solution having the following composition : xylose 74 %, mannose 2.9 %, arabinose 10.5 %, glucose 9.7 %, galactose 2.8 % and furfural 0.15 g/lit and a cellulosic residue having a dry weight of 0.565 kg that is, a yield of 70.7 % by weight of the original straw, and the following composition: alpha-cellulose 52.0 % hemicelluloses 13.8 % pentosans 5.0 % lignin 21.8 % and others 12.4 % and a degree of polymerisation of 820 glucose units.

Example 2

a) 0.8 kg of wheat straw was placed in a Teflon cage in an apparatus comprising a 5 lit reactor, a system to heat up the process water solution, a system to regulate flow and pressure and an efficient exchanger. 10 Litres of HNO_3 (0.3 % solution) were introduced at a pressure of 5 - 5.5 atm. at a temperature of 145°C and at a flow rate of 0.48 lit/minute. The solution kept in the reactor was purged with steam, followed by washing with water at 120 - 130°C and again purging with steam. There were collected 13.6 litres of solution containing 1.30 % reducing sugars, by weight, which corresponds to a yield of 22.8 % by weight, and a residue of 0.540 kg dry weight. The sugar solution after filtration and stripping with steam to remove the furfural it contained had the composition: xylose 71.2 %, mannose 1.7 %, arabinose 12.8 %, glucose 11.0 %, and galactose 3.2 %. This sugar solution to which were added the necessary nutrients, was used in the production of protein by a culture of *Candida utilis*. In a cycle of growth of 16 hrs. there was obtained a yeast yield of 65 % dry weight, based on the consumed sugars.

b) After a treatment as described above, in which a solution of sulfuric acid (0.5 %) at a flow rate of 0.8 lit/minute was used for the hydrolysis, there were obtained 13.5 litres of sugar solution containing 1.29 % reducing sugars, by weight or a yield of 22.6 % by weight, and a solid residue of 0.540 kg of dry weight. Under the same conditions of hydrolysis, but using a 0.3 % solution of sulfuric acid, there were obtained yields of 18.5 % in reducing sugars and of 70.5 % in cellulosic residue, having a degree of polymerisation of 830 glucose units.

Example 3

0.8 kg of wheat straw was placed in apparatus as described above and prehydrolysed using 10 litres of 0.5 HCl solution at a temperature of 140°C, and at a flow rate of 0.55 lit/minute. This was followed by purging with steam, washing with hot water at 120 - 130°C and again purging with steam. There were collected from the reactor and the pressing of the residue a total of 13.6 litres of solution having a concentration of reducing sugars of 1.3 %, by weight, corresponding to a yield of 20.7 %. The cellulosic residue had a dry weight of 0.550 kg, that is a yield of 68.8 % by weight based on the straw. Under the same processing conditions, except for the flow rate of the solution which was 0.92 lit/minute, were obtained yields of 15.5 % of reducing sugars and 74.0 % of cellulosic residue. A sugar solution produced as described above was filtered, treated with steam to remove the furfural it contained, and used as a nutrient for a culture of *Candida utilis*. The cycle of growth was 16 hrs and the yield in dry protein was 64.5 % based on the consumed sugars.

Example 4

In apparatus as described above was placed 0.8 kg of dry wheat straw, which had been partially hydrolysed according to Example 1a by using 13.4 litres of the sugar solution obtained in this Example 1a was used as the processing solution, after its HCl concentration

had been adjusted to 0.3 %. The solution at 80 - 85 °C was quickly heated to 145 °C and introduced at a flow rate of 0.56 lit/hour. Proceeding as described in Example 1a, there were obtained 15 lit of a solution containing 2.28 % reducing sugars, by weight, and a solid residue of 0.580 kg dry weight. After recycling twice more the solution containing above 2.28 % reducing sugars, which leaving the exchanger each time at 80 - 85 °C, was heated up to 145 °C, and used for the hydrolysis of 0.8 kg of dry straw, there were finally obtained 20 litres solution of 4.65% reducing sugars content by weight. The cellulosic residue was obtained in yields of 72.2 % and 73.5 %, respectively and both were found to be of the desired composition. A quantity of the above concentrated sugar solution was diluted to 2.3 % reducing sugars, filtered, stripped with steam to remove furfural, and was used as a nutrient for a culture of protein-producing *Candida utilis*. The cycle of growth was 15 hrs, the yield in dry yeast 64.5 % and approximately 90% of the sugars were consumed.

Example 5

a) In an autoclave of capacity 5 litres, lined with Teflon and equipped with an agitator and internal cooling coil, were placed 0.5 kg of dry wheat straw and 4 litres of 0.5 % HCl solution. The whole was heated, with stirring, to 130 °C in 20 minutes kept at that temperature for 20 minutes with stirring, and then cooled quickly. The product of the autoclave was drained from the solution and the solid part was washed with 2 litres of hot water at 60 - 70 °C, drained again and then pressed at 25 kg/cm^2. In total, 5.5 litres of solution containing 2.0 % reducing sugars, by weight, were collected representing a hydrolysis yield of 21 % and 0.355 kg of dry cellulose residue, that is, 70.0 % of the original straw, by weight. The solution had the composition : xylose 74.3%, mannose 5.2%, arabinose 11.8%, glucose 5.9%, galactose 2.9%, by weight, and furfural 0.13 gr/litres.

b) In the above autoclave were placed 0.8 kg of straw and 4 litres of 0.3 % HCl solution. The whole was heated up to 135 °C in 20 minutes and kept at that temperature for 20 more minutes. The product was pressed at 25 kg/cm^2 to produce, in total, 3.5 lit. of solution containing 3.2 % of simple reducing sugars (representing a yield in hydrolysis of 16 %): The pressed product was washed with 4 litres of hot water (70 °C), with stirring and pressed at 25 kg/m^2. 3.6 litres of dilute sugar solution were obtained which contained 0.9 % of simple reducing sugars.

c) In accordance with a treatment as described above, the autoclave was charged with 0.8 kg of dry straw and the 3.6 lit. of dilute sigar solution of Example 5b, after adding 0.5 lit. of water, and hydrochloric acid solution so that the process solution contained 0.3 % HCl by weight. After heat processing at 135 °C, as described above, the product was pressed at 25 kg/m^2 producing 3.6 litres of sugar solution with 4.25 % reducing sugars (hydrolysis 16 %). The solid residue was washed with 4 litres of hot water (70 °C) with stirring, and was pressed again at 25 kg/m^2 to produce 3.8 litres dilute sugar solution containing 1.00 % simple reducing sugars. This dilute solution after recycling gave concentrated sugar solutions.

Example 6

Using the autoclave of Example 5, a series of hydrolysis runs were performed using 0.5 kg of dry wheat straw, each time under different processing conditions, with the following results:

a) The hydrolysis treatment was performed using 4 litres of 0.5 % H_2SO_4 at 130 °C, according to a procedure of heating up to 130 °C in 20 minutes and keeping at that temperature for 60 minutes with stirring. After draining the solution, washing and pressing the solid residue, there were obtained 5.65 litres of a solution with 2.05 % reducing sugars, by weight, and a solid product of 0.330 kg, dry weight, having a moisture content of 40 - 45 %, by weight. Processing as described in Example 6a in all respects except for the catalytic strength of the solution, which was reduced to 0.3 % in H_2SO_4, gave a solution containing 1.30 % reducing sugars and a cellulosic residue having a dry weight of 0.352 kg, and a moisture content of 45 - 50 %, by weight. A quantity of the above sugar solutions containing 1.8 % of reducing sugars, was used as nutrient in the production of a microbe culture which produced protein. The cycle of growth was 18 hrs and the yield in dry yeast was 61 % based on the consumed sugars of which 87 % were utilised.

b) The hydrolysis treatment was performed using 4 litres of 0.5 % $HClO_4$ solution but in all other respects according to Example 6a). There were obtained 5.63 litres of sugar solution containing 2.03 % reducing sugars and 0.350 kg of dry cellulosic residue having a moisture content of 40 - 45 %, by weight, and a degree of polymerisation of 825 glucose units.

c) The prehydrolysis treatment was performed using 4 litres of a 0.35 % HNO_3 solution but in all other respects in accordance to Example 6a). There were obtained 5.6 litres of solution containing 2.08 % reducing sugars and a cellulosic residue having a dry weight of 0.340 kg, a moisture content of 50 %, by weight, and a degree of polymerisation of 810

glucose units.
d) The prehydrolysis treatment was conducted using 4 litres of 0.5 M phosphoric acid solution but otherwise as described in Example 6a). There were obtained 5.6 litres of sugar solution containing 2.05 % simple reducing sugars and a cellulosic residue having a dry weight of 0.340 kg dry weight, a moisture content of 50 %, and a degree of polymerisation of 825 glucose units.

Example 7

Into each of 5 flasks of 5 litres capacity, with reflux condesers, designated as I, II, III, IV, V, were placed 0.5 kg of wheat straw and 4 litres of processing solution. The type and concentration of catalysts used were : flask I, HCl, 0.5 M; II H_2SO_4 0.25 M; III H_2SO_4 0.5 M; IV $HClO_4$ 0.5 M; and V HNO_3 0.5 M. All were heated up to boiling and at the 2nd and 3rd hour samples were taken (I-2, I-3 etc., where the numbers 2 and 3 indicate the hours of boiling when the sample was taken) and examined for the sugar content from which it was concluded that the degree of hydrolysis, based on the initial straw (%) was:
I-2 17.8% II-2 7.3% III-2 16.7% IV-2 17.1% V-2 17.9%
I-3 23.9% II-3 10.9% III-3 23.1% IV-3 22.9% V-3 23.4%

With the above results it was shown, as was also observed in the hydrolysis treatment at higher temperatures (Example 1, 2 and 5), that the acid catalysis is of the molecular type, that is, its effect depends on the molecular concentration of the acid and not on the hydrogen ion concentration. The sugar solutions according to their time of boiling and the resultant degree of solubilisation had the composition found in the preceding examples. The catalytic strength of the acids H_3PO_4, $ClCH_2COOH$ and p-CH_3-C_6H_4-SO_3H was also studied and it was found that after 3 hrs of boiling, the degree of hydrolysis was 23.0, 22.2 and 21.9 % respectively. Using a 0.5 M SO_2 solution in a run, in the autoclave at 100 °C, for 3 hrs, sugars were produced corresponding to 22.0 % of hydrolysis.

Example 8

In the autoclave used in Example 5, following the procedure described in that Example, barley and rice straws and an alfalfa variety were subjected to prehydrolysis under the following conditions and with the following results:
a) 0.5 kg of barley straw were subjected to a prehydrolysis treatment using 0.5 % HCl solution at 130 °C under conditions such that the heating to 130 °C took 20 minutes and the solution was kept at that temperature with stirring for 30 minutes. After draining, washing and pressing the solid product there were obtained 5.7 litres of solution containing 1.90 % reducing sugars, by weight, equal to a yield of 21.6 %, and a cellulosic residue having a dry weight of 0.335 kg and a moisture content of 45 % by weight. The cellulosic residue had the composition : alpha-cellulose 52.3%, hemicelluloses 13.4%, lignins 24.0%, ash and extractables 10.3%. The sugar solution was found suitable for the growth of protein-producing microorganisms.
b) 0.5 kg of rice straw were treated for partial hydrolysis using 4 litres of 1.3 % HCl solution at 100 °C. After boiling for 2 hours, the yield of reducing sugars was 21.0 % based on the straw. The solid residue was drained, washed with 2 litres of hot water, drained again and compressed at 25 kg/cm^2. The combined solutions totalled 5.6 litres and contained 1.87 % reducing sugars by weight. The solid residue had a dry weight of 0.325 kg and the following composition: alpha-cellulose 50.8%, hemicelluloses 13.1%, lignin 25.0%, ash and extractables 11.1%. The sugar solution examined was found to be very suitable for fermentation by protein-producing microorganisms.
c) 0.5 kg of alfalfa (dry weight), were hydrolysed using 4 litres of 1.5 % H_2SO_4 at 100 °C. After boiling for 3 hrs, the solid residue was drained, washed with 2 litres of hot water and compressed to a cellulosic product having a dry weight of 0.330 kg. The alpha-cellulose content of that residue was 50.8 %, by weight.

Example 9

In an autoclave of 5 litres capacity were charged 0.8 kg of prehydrolysed straw (produced by a hydrolysis which resulted in a 18% yield in sugars: Examples 1 and 2) together with 4 litres pulping solution having the composition : 0.120 kg Na_2SO_3, and 0.040 kg of NaOH, for the production of an alkaline sulfite pulp. The prehydrolyzed straw was kept within two plates having holes for the circulation of the solution, in such a way, that the pulp was permanently fully covered with solution. The whole was then heated in 2 hours to 160 °C and kept for 6 further hours at this temperature. After cooling, the pulp was separated and washed with excess water, and then subjected to beating in a mill to separate the fibres. It was then passed through a diaphragm to separate the unprocessed parts, representing 3 % by weight, which after collection were recycled. The pulp was obtained in a yield of 42% based on the initial straw or a yield of 59 % based on the prehydrolysed straw and had a

permanganate number of 15.0 corresponding to a lignin content of 3.6 %, by weight. After testing, the pulp was found to have very good mechanical and paper making properties. The production of pulp according to the above, but with heating to 150 °C within 2 hrs and keeping at that temperature for 8 hrs, gave a pulp of very satisfactory paper making properties at a yield of 43.2 % and having a permanganate number of 17.0 corresponding to a lignin content of 4.2 %, by weight.

The pulps of the above quality are self sufficient to make paper of satisfactory properties. By increasing or decreasing the amount of chemicals and temperature and time of processing, there are obtained pulps containing higher or lower than optimum quantities of lignin and consequently in higher or lower yields. These qualities are not always self sufficient, but after mixing produce paper of satisfactory quality. In general, self sufficient quantities of pulp prepared as above have a permanganate number of 10 - 20, that is, contain lignin in quantities of 2 - 5 %. The alkaline sulfite pulps obtained according to the above procedure are usually of good colour quality. To improve the colour quality they are decolorised with calcium hypochlorite, for example at 30 °C for 2 hours, in a solution containing 9.0 % of chlorine, by weight. This treatment results in a pulp of excellent colour and having very satisfactory paper making properties, with a weight loss of only 3.0 % (based on the initial straw). The pulps of the above type mixed with 10 - 15 % by weight of mechanical wood pulp, give a product for paper of improved writing properties.

Example 10

In the autoclave of 5 litres capacity used in Example 9 were placed 0.8 kg of prehydrolysed straw having a moisture content of 50% (produced by a hydrolysis resulting in a 16% yield of sugars) between two plates having holes and subjected to kraft pulping using 4 litres of solution having the composition : 0.110 kg NaOH and 0.05 kg of Na_2S, by heating at 160°C for 3 hours. After cooling, the pulp was separated from the solution, washed with excess of water, and beaten in a mill to separate the fibres. It was then passed through a diaphragm to separate the unprocessed parts, representing 5 % by weight, which were collected and recycled. A pulp of the kraft type was obtained in a yield of 42 %, based on the initial straw, or 55.0 % based on the prehydrolysed straw, having a permanganate number of 14.0 corresponding to a lignin content of 2.5 % by weight based on the pulp. The pulp had a satisfactory colour and good mechanical properties, with characteristics of a kraft type wood pulp. A treatment as described above, but with heating to 145°C for 5 hours, gave a pulp having satisfactory properties as above with a permanganate number of 16.5 corresponding to a lignin content of 4.0 %, by weight, based on the pulp.

Pulps of satisfactory kraft characteristics obtained from the treatment as described above are those having a permanganate number of between 10 to 20 which correspond to a lignin content of 2 - 6 % by weight, based on the dry pulp. Smaller or greater quantities of chemicals and longer or shorter times of processing than normal, give pulps which cannot produce good quality paper, in either lower or higher yields depending on how low or high is the amount of lignin present. Those having a low content in lignin are suitable for the production of regenerated cellulose whereas those having a high content in lignin are good for wrapping and packaging. To improve the colour of the good quality pulps they are decolorised using a solution of calcium hypochlorite. With 70 gr of chlorine per kg dry pulp in the decolorising solution and treatment at 30 °C for 2 hrs, there are obtained pulps of satisfactory colour quality. The decolorising causes a weight loss in the pulp of 2.2 % by weight (based on the initial straw).

Example 11

In the autoclave used in Example 9 was placed successively 0.8 kg of dry weight prehydrolysed straw which was subjected to kraft pulping with processing solutions, where the Na_2S and NaOH are partially replaced by Na_2SO_3. In four such runs, the effect of the degree of substitution by Na_2SO_3 on the yield and the quality of the pulp was examined. The following solutions and conditions of treatment were used:

a) A solution of Na_2SO_3 0.040 kg, Na_2S 0.112 kg and NaOH of 0.233 kg, per kg of dry pulp, processing at 160 °C for 3 hours.

b) A solution of Na_2SO_3 0.080 kg, Na_2S 0.100 kg and NaOH 0.205 kg, per kg of dry pulp and processing at 160 °C for 3.5 hrs.

c) A solution of Na_2SO_3 0.120 kg, Na_2S 0.088 kg and NaOH 0.177 kg, per kg of dry pulp, processing at 160 °C for 4 hours.

Progressing from a→c the pulps obtained showed a yield improvement of from 42 to 44 % and also a colour improvement. There was observed in the results obtained from a→c, a progressing change in the kraft characteristics. The lignin content was in a) 4.8 % and in c) 2.5 % by weight. All these pulps were of satisfactory mechanical and paper making properties.

Example 12

A flask of 5 litres capacity was used which was equipped with a stirrer, a system for introducing chlorine external cooling with running water. Into this flask was placed 0.4 kg of prehydrolysed straw (dry weight) obtained by a hydrolysis which resulted in a 23 % yield by weight of sugars. The prehydrolysed straw had a moisture content of 5 % by weight. After slow and careful agitation, the mass became homogeneous and then chlorine gas was introduced at a flow rate of 2 litres/minute and at a constant temperature of 30 °C. After 10 minutes of chlorine flow, the prehydrolysed straw had become homogeneously pink in colour. An absorption of 0.35 kg of Cl_2 per kg of dry pulp was recorded. To complete the chlorination, the mixture was agitated for 60 minutes and after this, it was poured into 10 litres of water. The solid residue was drained and washed with a 3 % NaOH solution, followed by water washing until it was neutral. The pulp was thus delignified to the right extent and was of a quality suitable for use. It was obtained in a yield of 48 - 51 % by weight based on the initial straw, and had a lignin content of 4.3 % by weight. The colour of the pulp was very satisfactory but after a mild decoloration treatment, improved further. The weight loss on decoloration was 3 % by weight, based on the initial straw. By changing the quantity of absorbed chlorine, by 20 %, the lignin content was further lowered by 50 - 60 % and the yield dropped by 2 - 2.5 %. On the other hand, by reduction of the absorbed chlorine by 20 %, the lignin content was further increased by 100 - 150 % and the yield in pulp increased by 2 - 3 % units. With the above examples it is shown that delignification with chlorine is a special treatment for pulping the prehydrolysed straw of this invention and that the improved results in quality and in yield of pulp are determined by treatment conditions which are narrowly defined.

Example 13

Prehydrolysed straw resulting from a hydrolysis which produced a yield of less than 23 % of sugars was successfully used in the production of pulp under the following conditions:
a) Prehydrolysed straw, resulting from a hydrolysis which produced a yield of 19% of sugars was pulped according to Example 9 with an alkaline sulfite solution to give a pulp which, after decolorising, was obtained in a yield of 41.5 % based on the initial straw. This pulp had satisfactory paper making properties.
b) Prehydrolysed straw resulting from a hydroylsis which produced a yield of 15.6 % of sugars was pulped according to Example 10, to kraft pulp. A pulp of satisfactory colour and mechanical properties containing 2.6 % lignin was obtained. After mild decolorising, it was shown to be suitable for making paper of good quality.

Example 14

a) The cellulosic residue from prehydrolysis treatment of alfalfa grass of Example 8c, was pulped to produce a kraft pulp according to Example 10 at a temperature of 150 °C for 4 hours. The resulting pulp was drained, washed with excess water, beaten in a mill, and in the form of a dilute solution, passed through a diaphragm to separate the unprocessed material. The pulp thus obtained was of satisfactory colour, containing 3.2 % lignin by weight and, after decolorising, was found to be a good material for manufacturing regenerated cellulose.
b) The cellulosic residue obtained from the prehydrolysis treatment of barley straw described in Example 8a was pulped to produce a sulfite pulp according to Example 9. After mild decolorising, the pulp was obtained in a yield of 40 % based on the initial straw, having a lignin content of 1.5% and satisfactory paper making properties.
c) The cellulosic residue of the prehydrolysis treatment of rice pulp of Example 8b was pulped with chlorine as described in Example 12 to an uptake of chlorine of 0.30 kg/kg dry pulp. After washing successively with water, 1 - 3 % sodium hydroxide solution, and again water to neutralise it, and after mild decolorising a pulp of excellent colour quality was obtained. The pulp had a content of 1.4 % lignin, by weight, and was suitable for making paper of excellent quality.

WHAT WE CLAIM IS:

1. A process for the production of monosaccharides and a cellulosic-rich material which comprises subjecting straw for 10 - 180 minutes to a selective pre-hydrolysis treatment in the presence of one or more acid catalysts at a temperature of from 100 to 160°C under pressure until the easily hydrolysable constituents of the straw such as pentosans, starch and hemicelluloses are converted substantially into monosaccharides in a yield representing 15-23 % by weight of the straw, and until a residue rich in cellulose is obtained in a yield representing 68-76 % by weight of the straw, said residue being suitable for processing to chemical pulp and to pure cellulose.

2. A process as claimed in claim 1 wherein the straw is a cereal straw which after the prehydrolysis treatment produces fermentable sugars together with a material rich in

cellulose suitable for the production of chemical pulp and of pure cellulose.

3. A process as claimed in claim 2 wherein the cellulosic residue has a content of 52 - 58 % by weight alpha-cellulose and the acid catalyst is an inorganic or organic acid.

4. A process as claimed in any of claims 1 to 3 wherein the catalyst is selected from at least one of the following: H_2SO_4, sulphurous acid, HCl, HNO_3, H_3PO_4, $HClO_4$, $ClCH_2COOH$ or p-CH_3-C_6H_4-SO_3H.

5. A process as claimed in claim 4 wherein the catalyst is used at a concentration of 0.1 - 1 % by weight based on the total acid solution.

6. A process as claimed in any of claims 1 to 5 wherein the cellulosic residue, after the prehydrolysis treatment, is washed with water and/or with a 1 - 3 % by weight sodium hydroxide solution and thereafter is compressed to a product having a moisture content of 40 - 50 % by weight.

7. A process a claimed in claim 6 wherein the solution obtained after hydrolysis and the washing solution and the solution obtained after compression are mixed to form a solution having a concentration of 1.2 - 5.0 % by weight in sugars, which after adjusting to the original catalytic strength is recycled as a whole or partly as hydrolysis solution until a final concentration of 6 - 8 % by weight in sugars, is obtained and 90 - 95 % of the sugars in the final concentrated solution are monosaccharides.

8. A process as claimed in any of claims 3 to 7 wherein the composition of the sugar in the hydrolysis solution is: xylose 67 - 75 %, mannose 1.2 - 5.0 %, arabinose 10 - 18 %, glucose 5 - 12 %, galactose 2 - 4 %, and the cellulosic residue composition is: alpha-cellulose 52 -54 %, hemicelluloses 11 - 13 %, lignin 21 - 23 %, extractables 10 - 13 %, and ash 5 - 6 %, all the percentages being by weight, and a degree of polymerisation of 790 - 830 glucose units.

9. A process for the production of chemical pulp wherein the cellulosic residue obtained in a process as claimed in any of claims 1 to 8 in which the yield of sugars was 17 - 20 % by weight, is treated with an alkaline solution of sulfite salts, and then heated within two hours up to 150 - 160°C and maintained at that temperature for 5 - 6 hours.

10. A process as claimed in claim 9 wherein the alkaline solution of sulfite salts contain 225 kg Na_2SO_3 and 8.5 kg NaOH per ton of dry pulp.

11. A process for the production of kraft pulp wherein the cellulosic residue obtained in a process as claimed in any of claims 1 to 8 in which the yield of sugars was 15 - 19 % by weight, is treated with a kraft pulping solution containing Na_2S and NaOH and with a pulping solution in which Na_2S and NaOH are partially replaced by Na_2SO_3, and then heated up to 150 - 160 °C and maintained at that temperature for 4 - 6 hours.

12. A process as claimed in claim 11 wherein the kraft pulping solution contains 125 kg Na_2S and 260 kg NaOH per ton of dry pulp.

13. A process as claimed in claim 11 or 12 wherein the pulping chemicals Na_2S and NaOH are partially replaced by Na_2SO_3 in a quantity of 0.1 to 30 % by weight.

14. A process as claimed in any of claims 1 to 8 wherein the cellulosic residue of straw prehydrolysis after hydrolysis to 20 - 23 % by weight in sugars, is treated with chlorine in a horizontal slow rotating reactor or a slowly agitated reactor of the vertical type, until up to 20 % by weight of chlorine based on the prehydrolysis residue treated is absorbed, and is subsequently washed with water and alkaline solution until neutral.

15. A process for the production of chlorine pulp wherein the residue obtained in a process as claimed in any of claims 1 to 8 is washed with a 1 - 3 % by weight solution of NaOH before pulping in order to obtain a pulp of improved colour quality.

16. A process as claimed in any of claims 1 to 15 wherein the pulp is decolorised with calcium hypochlorite in a mild treatment resulting in a weight loss of only 2 - 3 % by weight.

17. A process as claimed in any of claims 1 to 16 wherein alfalfa or rice straw is subjected to the prehydrolysis treatment for the production of a cellulosic residue.

18. A process as claimed in any of claims 1 to 17 wherein in the prehydrolysis there are obtained monosaccharides in quantities of from 15 % to 23 %, pulp up to 51 % and lignin up to 13 % by weight, based on the initial straw.

19. A process as claimed in claim 1 substantially as described with specific reference to any one of the Examples.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.